The pseudoazurin isolated from *A. cycloclastes* IAM 1013 was purified according to the methods reported already.[3,4] The absorbance ratio of A_{282}/A_{594} was 1.45. The complete Cu depletion was carried out by dialyses (twice) of the pseudoazurin solution against 0.1 M Tris-HCl buffer (pH 8.0) containing KCN (0.01 M). Cobalt(II)-substituted pseudoazurin was prepared by anaerobic incubation of apopseudoazurin (0.49 μmol) and $CoCl_2$ (5 μmol; Co in 99.999% purity) in 2 mL of 0.1 M Tris-HCl buffer (pH 8.0) for 6 days at 4 °C. The excess cobalt ion was removed by dialysis against 0.1 M Tris-HCl (pH 8.0) for 5 h and the resulting Co(II)-pseudoazurin was concentrated for spectroscopic measurement. The concentration of cobalt in Co(II)-pseudoazurin was determined to be 0.8 mM (Co/protein = 1) by measurement with an atomic absorption spectrophotometer.

The electronic, CD, and MCD spectra of Co(II)-pseudoazurin at room temperature are represented in Figure 2. The electronic absorption spectrum in the range of 300-500 nm shows one absorption band at 335 nm and two shoulder bands at around 390 and 440 nm. In the same region, the CD and MCD spectra manifest three and four extrema, respectively. These absorption, CD, and MCD bands demonstrated that there is one cysteinyl ligand around cobalt(II) responsible for a $S^- \rightarrow Co(II)$ charge transfer, as described in the other Co(II)-substituted blue copper proteins (Table I). This finding corresponds with the results of the amino acid sequence and the X-ray crystallographic analysis of *Alcaligenes* pseudoazurin.[25] The visible absorption peaks at 505 and 673 nm and the shoulder band near 640 nm (ϵ = 240-270 $M^{-1}\ cm^{-1}$ are assigned to the d-d transitions ($^4A_4(F) \rightarrow {}^4T_1(P)$) for the distorted tetrahedral Co(II) ion,[33,38] which are compared with the d-d transitions for several Co(II)-substituted proteins in Table I. The negative pattern of the MCD spectrum at 600-700 nm is likewise compatible with tetrahedral symmetry for the high-spin Co(II) ion.[33,38] In Table I, the spectral data of co-(II)-substituted *Achromobacter* pseudoazurin are similar to those of the Co(II) derivatives of two plastocyanins and especially cucumber plantacyanin, but they are a little different from those of the Co(II) derivatives of two azurins and stellacyanin. Moreover, the CD and MCD spectra of Co(II)-pseudoazurin in Figure 2 also display more of a resemblance to those of Co-(II)-plastocyanin and Co(II)-plantacyanin than to those of Co-(II)-azurin and Co(II)-stellacyanin.[33,34,37]

The Co(II) substitution of pseudoazurin implies that the donor set of the copper site in native pseudoazurin is in accord with that of cucumber plantacyanin and the structure of the copper site is essentially more analogous to those in cucumber and bean plastocyanins rather than that in bacterial azurin. According to the X-ray crystallographic analyses of plastocyanin[26,27] and azurin,[11,28-30] the copper site of plastocyanin was determined to be a very distorted tetrahedral arrangement with three in-plane, strongly bound ligands (two imidazole nitrogens and one cysteinyl sulfur, CuN_2S) and one axial, weakly bound sulfur ligand, methionine.[26] However, in azurin, a distorted trigonal-planar geometry (CuN_2S) with two weakly interacting groups (methionyl sulfur and the peptide carbonyl oxygen of a glycine residue) in axial positions completing an axially elongated trigonal bipyramid was confirmed.[11,30] The spectroscopic difference between Co-(II)-plastocyanin and Co(II)-azurin could be associated with the above geometrical differences in the native forms.

As mentioned above, the intense absorption bands near 450 nm and the rhombic-type EPR signals of native pseudoazurin and plantacyanin[39] are distinct from the weak corresponding absorption band and the axial-type EPR signal of native plastocyanin. On the other hand, the metal sites in the Co(II) derivatives of pseudoazurin and plantacyanin are geometrically similar to that in Co(II)-plastocyanin. This suggests that the axial binding of methionine sulfur to the distorted trigonal-planar CuN_2S moiety in pseudoazurin or plantacyanin may be stronger than that in plastocyanin. It seems likely that the axial bonds in the copper sites of pseudoazurin and plantacyanin, which are shorter than that in plastocyanin, cause a rhombic EPR signal attributable to a distorted tetrahedral copper(II) and contribute to the high absorptivity of the band near 450 nm. The 455-nm band of *Achromobacter* pseudoazurin consists of two transitions exhibiting two CD extrema at 400 and 464 nm; at least one of the two transitions is probably due to a S(Met) → Cu charge-transfer transition,[36,40] although an alternative assignment to N(His) → Cu charge transfers is considered a possibility.[40,41] Native stellacyanin also shows a rhombic EPR spectrum. However, the spectroscopic properties of Co(II)-stellacyanin are different from those of Cu(II)-pseudoazurin, which is likely related to the absence of methionine in the coordination sphere of stellacyanin.[2]

Registry No. Cys, 52-90-4; Co, 7440-48-4; Cu, 7440-50-8.

---

(33) Solomon, E. I.; Rawlings, J.; McMillin, D. R.; Stephens, P. J.; Gray, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 8046-8048.

(34) Sakurai, T. *Biochem. Biophys. Res. Commun.* **1986**, *139*, 961-966.

(35) Suzuki, S.; Sakurai, T.; Nakahara A.; Masuko, M.; Iwasaki, H. *Biochim. Biophys. Acta* **1985**, *827*, 190-192.

(36) Tennent, D. L.; McMillin, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 2307-2311.

(37) Suzuki, S.; Yasui, S.; Kawahara, K.; Sakurai, T.; Okamoto, H.; Sawada, S.; Hirose, S.; Nakahara, A.; Yang, W. *Sci. Rep., Coll. Gen. Educ. Osaka Univ.* **1985**, *34*, 1-6.

(38) Vallee, B. L.; Holmquist, B. In *Methods for Determining Metal Ion Environments in Proteins*; Darnall, D. W., Wilkins, R. G., Eds.; Advances in Inorganic Biochemistry, Vol. 2; Elsevier: New York; p 27-74.

(39) In the absorption spectrum of cucumber plantacyanin, the value at 443 nm was reported to the 2030 $M^{-1}\ cm^{-1}$: Murata, M.; Begg, G. S.; Lambrou, F.; Leslie, B.; Simpson, R. J.; Freeman, H. C.; Morgan, F. J. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 6434-6437.

(40) Penfield, K. W.; Gay, R. R.; Himmelwright, R. S.; Eickman, N. C.; Norris, V. A.; Freeman, H. C.; Solomon, E. I. *J. Am. Chem. Soc.* **1981**, *103*, 4382-4388.

(41) Fawcett, T. G.; Bernarducci, E. E.; Krogh-Jespersen, K.; Schugar, H. J. *J. Am. Chem. Soc.* **1980**, *102*, 2598-2604.

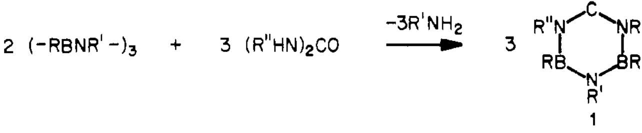
Contribution from the Department of Chemistry,
University of Kentucky, Lexington, Kentucky 40506-0055

Reactions of *N*,*N'*-Dimethylurea with Boron-Nitrogen Compounds[1]

L. Komorowski† and K. Niedenzu*

Received August 30, 1988

Only two studies on the interaction of boron-nitrogen compounds with ureas are known. First, the reaction of borazines, $(-RBNR'-)_3$, with urea as well as *N*-mono- and *N*,*N'*-diorganyl derivatives thereof has been described to proceed according to eq 1. The resultant 1,3,5-triaza-2,4-diboracyclohexan-6-one



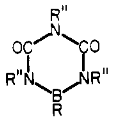
(1)

(=ketotriazadiborinane) species **1** (obtained in 55-65% yield) were characterized by elemental analysis only.[2] Several compounds containing the same structural skeleton of **1** and related species such as **2** and **3** were found among the reaction products of haloorganylboranes with N-organo-substituted ureas as well as N-lithiated[3] or N-silylated[4,5] derivatives of the latter.

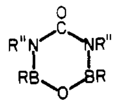
---

† On leave of absence from the Technical University of Wrocław, Wrocław, Poland.

0020-1669/89/1328-0804$01.50/0 © 1989 American Chemical Society



2



3

In another study, equimolar amounts of *N,N'*-dimethylurea, $(R''HN)_2CO$ ($R'' = CH_3$), and tris(dialkylamino)boranes, $B(NR'_2)_3$ ($R' = CH_3$, C_2H_5), were found to react in boiling xylene to give good yields of 1,5-diaza-2,4-dibora-3-oxacyclohexan-6-ones (3).[4]

The present work is concerned with a study of the reaction of *N,N'*-dimethylurea with various types of boron–nitrogen compounds containing trigonal boron.

Experimental Section

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorrected) were determined on a Mel-Temp block.

NMR spectra were recorded for solutions in $CDCl_3$ (unless otherwise noted) on a Varian XL-200 or VXR-400 (^{11}B) or GEMINI-200 (^1H, ^{13}C) instrument. Chemical shift data are given in ppm with positive values indicating downfield from the reference (internal $(CH_3)_4Si$ for ^1H and ^{13}C NMR, external $(C_2H_5)_2O\cdot BF_3$ for ^{11}B NMR). Abbreviations are as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, m = unresolved multiplet. An asterisk denotes a broad signal. Coupling constants *J* are given in hertz. All ^{13}C NMR spectra were recorded in the proton-decoupled mode. Mass spectral data (70 eV unless otherwise noted) were recorded on a VG ZAB-2F spectrometer; data are given to *m/z* 30 for 5% or greater relative abundances (in parentheses) only.

$C_2H_5B(\mu\text{-}NH)(\mu\text{-}NCH_3CONCH_3)BC_2H_5$ (1a; $R = C_2H_5$, $R' = H$, $R'' = CH_3$). A mixture of 11.7 g (71 mmol) of tri-*B*-ethylborazine, $(-C_2H_5BNH-)_3$,[6] and 9.4 g (107 mmol) of *N,N'*-dimethylurea was heated in an oil bath at 200 °C for 6 h. After it was cooled to room temperature, the material solidified. It was extracted with several portions of ether to leave a polymerlike brown residue (which was not further investigated). The ether was evaporated from the clear solution, and the colorless solid residue was recrystallized from pentane to give 9.4 g (48%) of product, mp 95–98 °C. Anal. Calcd for $C_7H_{17}B_2N_3O$ ($M_r = 180.85$): C,46.48; H, 9.47; B, 11.95; N, 23.23; O, 8.85. Found: C, 46.35; H, 9.45; B, 9.73; N, 22.98. NMR data: $\delta(^1H)$ 5.25* (1 H, s), 3.01 (6 H, s), 1.02 (10 H, s); $\delta(^{11}B)$ 36.2 ($h_{1/2} = 265$ Hz); $\delta(^{13}C)$ 160.0, 30.8, 8.0, 7.5*. Mass spectrum: *m/z* 181 (49), 180 (100), 179 (41), 178 (6), 153 (6), 152 (11), 151 (5), 123 (13), 122 (6), 95 (7), 94 (5), 68 (5), 67 (7), 66 (9), 40 (7), 38 (5).

$C_2H_5B(\mu\text{-}NCH_3)(\mu\text{-}NCH_3CONCH_3)BC_2H_5$ (1b; $R = C_2H_5$, $R' = R'' = CH_3$) was prepared in a fashion analogous to that for the preceding compound by reaction of 5.5 g (27 mmol) of tri-*B*-ethyl-tri-*N*-methylborazine, $(-C_2H_5BNCH_3-)_3$,[6] with 3.5 g (40 mmol) of *N,N'*-dimethylurea (5 h at 180 °C bath temperature). The resultant product was distilled under vacuum to give 5.4 g (70%) of the desired product, bp 115 °C (1 Torr). Anal. Calcd for $C_8H_{19}B_2N_3O$ ($M_r = 194.88$): C, 49.31; H, 9.83; B, 11.09; N, 21.56; O, 8.21. Found: C, 49.06; H, 9.87; B, 10.82; N, 21.43. NMR data: $\delta(^1H)$ 3.11 (6 H, s), 2.99 (3 H, s), 1.2–0.9 (10 H, m); $\delta(^{11}B)$ 36.7 (s, $h_{1/2} = 280$ Hz); $\delta(^{13}C)$ 159.0, 32.2, 31.2, 6.5*. Mass spectrum: *m/z* 196 (14), 195 (60), 194 (100), 193 (36), 192 (17), 181 (5), 168 (10), 167 (13), 166 (16), 165 (15), 137 (16), 136 (8), 125 (6), 109 (14), 108 (5), 81 (9), 80 (10), 68 (9), 66 (5), 52 (8), 51 (6), 44 (10), 40 (16), 32 (22).

$CH_3N(\mu\text{-}BC_6H_5)(\mu\text{-}CONCH_3CO)NCH_3$ (2; $R = C_6H_5$, $R'' = CH_3$). A mixture of 1.0 g (2.8 mmol) of tri-*B*-phenyl-tri-*N*-methylborazine, $(-C_6H_5BNCH_3-)_3$,[6] and 2.0 (22.7 mmol) of *N,N'*-dimethylurea was carefully melted and then boiled for 10 min. After the mixture was cooled to room temperature, 200 mL of benzene was added and the mixture was refluxed with stirring for 15 min. The clear solution was decanted from a small amount of insoluble material, and benzene was evaporated. Unreacted urea was sublimed off under vacuum (80 °C bath temperature). The residue was dissolved in 50 mL of benzene, insoluble material was discarded, and benzene was evaporated. The remaining solid was sublimed under vacuum to give 1.6 g (62%) of product, mp 126–128 °C, identical (NMR) with the previously described material[7] (obtained from $[(CH_3)_2N]_2BC_6H_5$ with *N,N',N''*-trimethylbiuret).

$CH_3B[\mu\text{-}N(CH_3)_2](\mu\text{-}NCH_3CONCH_3)(\mu\text{-}NCH_3CONHCH_3)BCH_3$ (4a). A mixture of 1 g (11.4 mmol) of *N,N'*-dimethylurea, 2 g (17.6 mmol) of bis(dimethylamino)methylborane, $[(CH_3)_2N]_2BCH_3$,[8] and 100 mL of toluene was refluxed with stirring for 9 h. Toluene was evaporated from the clear solution under reduced pressure. The solid residue (0.9 g, 59%) was recrystallized from acetonitrile to give a colorless product, mp 204–242 °C. Anal. Calcd for $C_{10}H_{25}B_2N_5O_2$ ($M_r = 268.93$): C, 44.66; H, 9.37; B, 8.04; N, 26.03; O, 11.90. Found: C, 44.73; H, 9.57; B, 7.97; N, 25.94. NMR data: $\delta(^1H)$ 4.9* (1 H, s), 2.81 (6 H, two closely spaced d), 2.71 (3 H, s), 2.59 (3 H, s), 2.15 (3 H, s), 2.11 (3 H, s), –0.06 (3 H, s), –0.07 (3 H, s); $\delta(^{13}C)$ 162.1, 158.9, 40.0, 31.8, 31.6, 31.0, 27.6, –0.6* (ratio for 162.1 and 158.9 signal ca. 1:2). Major ion peaks appear in the mass spectrum of the compound in the regions near *m/z* 269, 197, 168, and 125.

$C_2H_5B[\mu\text{-}N(CH_3)_2](\mu\text{-}NCH_3CONHCH_3)(\mu\text{-}NCH_3CONHCH_3)BC_2H_5$ (4b). A solution of 11.6 g (91 mmol) of bis(dimethylamino)ethylborane, $[(CH_3)_2N]_2BC_2H_5$,[8] in 50 mL of toluene was added dropwise with stirring to a hot solution of 4.0 g (45.5 mmol) of *N,N'*-dimethylurea in 100 mL of toluene. The mixture was refluxed overnight, and the solvent was evaporated under reduced pressure. The colorless residue was washed with pentane and then with ether to give 4.8 g (71%) of crude product, mp 226–228 °C (after recrystallization from acetonitrile). Anal. Calcd for $C_{12}H_{29}B_2N_5O_2$ ($M_r = 296.98$): C, 48.53; H, 9.84; B, 7.28; N, 23.57; O, 10.78. Found: C, 48.39; H, 10.12; B, 6.58; N, 24.35. NMR data: $\delta(^1H)$ 6.2* (1 H, s), 2.85 + 2.81 (6 H, two closely spaced d), 2.69 (3 H, s), 2.58 (3 H, s), 2.24 (3 H, s), 2.16 (3 H, s), 0.91 (6 H, q, *J* = 7.5), 0.68 (2 H, t, *J*= 7.5), 0.55 (2 H, t, *J* = 7.5) (the positions of the signals at 6.2 (up to 0.5 ppm) and 2.8 ppm (very slightly) are concentration-dependent); $\delta(^{11}B)$ 1.3 (s, $h_{1/2} = 635$ Hz); $\delta(^{13}C)$ 163.6, 159.9, 40.3, 40.0, 31.6, 31.3, 30.8, 27.5, 10.3, 9.8, 6.9*. The mass spectrum exhibits a weak parent ion cluster in the region *m/z* 297; the base peak is observed at *m/z* 211.

$C_6H_6B[\mu\text{-}N(CH_3)_2](\mu\text{-}NCH_3CONCH_3)(\mu\text{-}NCH_3CONHCH_3)BC_6H_5$ (4c). A mixture of 3.0 g (17.1 mmol) of bis(dimethylamino)phenylborane, $[(CH_3)_2N]_2BC_6H_5$,[9] 1.0 g (11.4 mmol) of *N,N'*-dimethylurea, and 80 mL of toluene was refluxed with stirring for 10 h. The colorless precipitate was collected, washed with pentane, and dried under vacuum to give 1.7 g (75% yield) of product A (=**4c**), mp 284–286 °C. Anal. Calcd for $C_{20}H_{29}B_2N_5O_2$ ($M_r = 393.10$): C, 61.11; H, 7.44; B, 5.50; N, 17.81; O, 8.14. Found: C, 60.06; H, 7.54; B, 5.40; N, 18.29. This material was readily soluble in chloroform (up to 3.7 wt %), and NMR spectra were recorded. NMR data: $\delta(^1H)$ 7.7 + 7.4 + 7.3 (10 H, unresolved m), 6.9* (1 H, s), 3.02 (3 H, d, *J* = 4.4), 3.00 (3 H, s), 2.84 (3 H, s), 2.64 (3 H, s), 2.20 (3 H, s), 1.68 (3 H, s); $\delta(^{11}B)$ 3.2 (s, $h_{1/2} = 250$ Hz); $\delta(^{13}C)$ 165.1, 161.5, 135.8, 134.9, 133.9, 127.3, 127.2, 127.0, 126.9, 41.4, 40.8, 34.4, 34.0, 33.7, 28.0. The mass spectrum exhibits a strong parent ion cluster in the region *m/z* 392.

The material A was recrystallized from chloroform/cyclohexane (1:1 by volume) to give a product that was analyzed as a 1:1 molar adduct of **4c** with chloroform, mp 278–280 °C. Anal. Calcd for $C_{21}H_{30}B_2Cl_3N_5O_2$ ($M_r = 512.55$): C, 49.21; H, 5.90; B, 4.22; Cl, 20.75; N, 13.66; O, 6.26. Found: C, 49.06; H, 6.08; B, 3.81; Cl, 19.57; N, 14.21.

This latter material B was considerably less soluble in chloroform (only up to 1.8 wt %) than the original material **4c**. However, the ^1H NMR spectrum was essentially identical with that of **4c** except that the signal of **4c** observed at 6.4 ppm is now located at 5.3* ppm (1 H) and an additional signal is observed at 1.43 ppm (1 H, s, position concentration dependent). An additional signal was also observed in the ^{13}C NMR spectrum (solution in CD_2Cl_2) at 78.0 ppm.

Reaction of *N,N'*-Dimethylurea with (Dimethylamino)diorganylboranes (Representative Reaction). A mixture of 6.0 g (42.5 mmol) of (dimethylamino)di-*n*-propylborane, $(CH_3)_2NB(n\text{-}C_3H_7)_2$,[10] and 1.0 g (11.4 mmol) of *N,N'*-dimethylurea was heated to reflux (190 °C bath temperature) with stirring. After about 1 h a clear homogeneous mixture was obtained and heating was continued for 45 h. A colorless precipitate formed on cooling of the reaction mixture to room temperature, and additional precipitate formed on addition of 40 mL of pentane. The

---

(1) Boron–Nitrogen Compounds. 118 (K.N.). Part 117: Das, M. K.; DeGraffenreid, A. L.; Edwards, K. D.; Komorowski, L.; Mariategui, J. F.; Miller, B. W.; Mojesky, M. T.; Niedenzu, K. *Inorg. Chem.* **1988**, *27*, 3085–3089.

(2) Boone, J. L. U.S. Patent 3 062 880, 1962.

(3) Maringgele, W. *J. Organomet. Chem.* **1981**, *222*, 17–32.

(4) Maringgele, W. *Chem. Ber.* **1982**, *115*, 3271–3289.

(5) Maringgele, W. *Z. Anorg. Allg. Chem.* **1980**, *467*, 140–148.

(6) Bielawski, J.; Das, M. K.; Hanecker, E.; Niedenzu, K.; Nöth, H. *Inorg. Chem.* **1986**, *25*, 4623–4628.

(7) Bielawski, J.; Niedenzu, K.; Weber, A.; Weber, W. *Z. Naturforsch., B: Anorg. Chem. Org. Chem.* **1981**, *36B*, 470–473.

(8) Nöth, H.; Fritz, P. *Z. Anorg. Allg. Chem.* **1963**, *322*, 297–309.

(9) Niedenzu, K.; Beyer, H.; Dawson, J. W. *Inorg. Chem.* **1962**, *1*, 738–742.

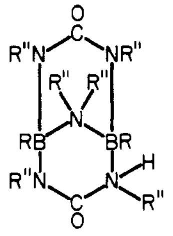
(10) Emerick, D. P.; Komorowski, L.; Lipinski, J.; Nahm, F. C.; Niedenzu, K. *Z. Anorg. Allg. Chem.* **1980**, *468*, 44–54.

precipitate was collected and was identified as *N,N,N'*-trimethylurea (78% yield): $\delta(^1H)$ 4.4* (1 H, s) 2.89 (6 H, s), 2.79 (3 H, d, $J = 4.7$). Pentane was distilled off the filtrate under reduced pressure, and the remaining liquid was fractionally distilled under vacuum to yield $(CH_3)HNB(n\text{-}C_3H_7)_2$ and the unreacted excess of $(CH_3)_2NB(n\text{-}C_3H_7)_2$.

Results

The reaction of *N,N'*-dimethylurea (=DMU) with borazines according to eq 1 has previously been reported in a patent,[2] but no experimental details are available. It has now been observed that no reaction occurred when several borazines, $(-RBNR'-)_3$ ($R = C_2H_5, C_6H_5$; $R' = H, CH_3$), were treated with the urea in heat-transfer media such as refluxing benzene, toluene, or xylene. However, heating of a neat mixture of the reactants to temperatures of 180–200 °C gave ready access to **1a** ($R = C_2H_5$, $R' = H$, $R'' = CH_3$) and **1b** ($R = C_2H_5$, $R' = R'' = CH_3$) originating from $(-C_2H_5BNR'-)_3$ with R' = H and CH_3, respectively. When $(-C_6H_5BNCH_3-)_3$ was heated with DMU to 200 °C, the mixture was not yet completely liquefied. Only at bath temperatures near 250 °C (boiling DMU) was a clear melt obtained and a reaction initiated. However, the resultant product consisted primarily of 1,3,5-triaza-2-boracyclohexane-4,6-dione (**2**) with $R = C_6H_5$ and $R'' = CH_3$. This result suggests that under the experimental conditions a condensation of DMU to *N,N',N''*-trimethylbiuret occurred first, and the latter reacted with the borazine to give the cited product. Compounds of type **2** have previously been obtained by transamination of bis(dimethylamino)organylboranes with biurets[7] and were also observed among the products of the condensation of dihaloorganylboranes with ureas.[3]

In the present work it was further found that bis(dimethylamino)organylboranes, $[(CH_3)_2N]_2BR$, react with DMU in a 1:1 molar ratio and with the release of only 1.5 equiv of dimethylamine to form diboron species. The process is independent of the ratio of the reactants. However, the products are most easily purified when an excess of the aminoborane is used. (No bis(ureido)boranes of the type $RB(NR'CONHR')_2$ could be obtained under the studied conditions, not even in the presence of a large excess of the urea). The resultant diboron species unexpectedly contained four-coordinate boron (as shown by ^{11}B NMR data), suggesting **4** as the structure of the species. This latter formulation is in complete consonance with all of the NMR data.



4a: $R = R'' = CH_3$
b: $R = C_2H_5$, $R'' = CH_3$
c: $R = C_6H_5$, $R'' = CH_3$

When a neat mixture of (dimethylamino)di-*n*-propylborane and DMU was refluxed (for 1–2 days) with an excess of the aminoborane as solvent, essentially quantitative conversion of DMU to *N,N,N'*-trimethylurea (=TMU) was observed in addition to the formation of (methylamino)di-*n*-propylborane. (Dimethylamino)diethylborane[11] did not react with DMU under analogous conditions (ca. 125 °C). However, with boiling xylene as solvent (ca. 140 °C) a reaction occurred that resulted again in an essentially quantitative conversion of DMU to TMU and of (dimethylamino)diethylborane to (methylamino)diethylborane within a period of 1 day. On refluxing of (the higher boiling) (dimethylamino)diphenylborane with DMU, a reaction occurred within a period of 15 h to again yield TMU and (methylamino)diphenylborane.

These observations illustrate that displacement of the dimethylamino groups of (dimethylamino)diorganylboranes by DMU in a transamination reaction does not occur readily. Rather, under the conditions used, DMU appears to decompose to methyl isocyanate and methylamine. Subsequently, methylamine exchanges with the dimethylamino group of the borane, and the generated dimethylamine interacts with the isocyanate to yield TMU. Indeed, an intermediate decomposition of *N,N'*-diorganylureas in the reaction with haloboranes has been noted earlier,[3] and displacement of dialkylamino groups of (dialkylamino)diorganylboranes by methylamine has been described as an exothermic reaction.[12]

In contrast, equimolar amounts of tris(dialkylamino)boranes, $B(NR'_2)_3$ ($R' = CH_3, C_2H_5$), and DMU have been reported to react in boiling xylene to give species of type **3** (with $R = NR'_2$ where $R' = CH_3, C_2H_5$).[4] Apparently, this latter reaction proceeds via the intermediate formation of the carbodiimide $CH_3N{=}C{=}NCH_3$ and the diboroxane (=diboryl oxide) $[(R'_2N)_2B]_2O$ (under release of 2 molar equiv of R'_2NH); the diboroxane then seems to react with a second DMU molecule in a transamination to yield a cyclic product of type **3**. In view of the observation that aminoboranes tended to react with DMU to form at least one $BNCH_3CONCH_3B$ unit, tris(dimethylamino)borane[13] was reacted with DMU in a 2:3 molar ratio in refluxing toluene (24 h). A glassy polymerlike material was obtained, the ^{11}B NMR spectrum of which showed at least four distinct resonance signals centered near 0 ppm (maxima at 2.4, –0.1, –1.0, and –1.4 ppm). The ^1H NMR spectrum of this product was inconclusive, and the 70-eV mass spectrum exhibited peaks up to m/z 572. This material was not further investigated.

Acknowledgment. This work was supported by the Office of Naval Research (K.N.).

---

(11) Alam, F.; Niedenzu, K. *Inorg. Synth.* **1983**, *22*, 209–211.

(12) Nöth, H.; Vahrenkamp, H. *Chem. Ber.* **1967**, *100*, 3353–3362.

(13) Niedenzu, K.; Dawson, J. W. *Inorg. Synth.* **1967**, *10*, 135–137.

Contribution from the Department of Chemistry
and Materials Research Laboratory, University of Illinois,
Urbana, Illinois 61801, and Crystalytics Company,
Lincoln, Nebraska 68501

Synthesis and Characterization of the Organozirconium and Organohafnium Complexes $[(\eta^5\text{-}C_5Me_5)MCl]_3O(OH)_3Cl$ and $[(\eta^5\text{-}C_5Me_5)MCl]_3O(OH)_4$

Laura M. Babcock,[†] Victor W. Day,*[,‡]
and Walter G. Klemperer*[,†]

Received June 13, 1988

We recently reported a synthesis of the tetrahedral $(Cp^*Ti)_4O_6$ molecule ($Cp^* = \eta^5\text{-}C_5Me_5$) by base-assisted hydrolysis of Cp^*TiCl_3.[1] In an attempt to prepare similar Cp*Zr and Cp*Hf cage compounds, we have hydrolyzed Cp^*ZrCl_3 and Cp^*HfCl_3 in the presence of triethylamine. Unlike the titanium system, the zirconium and hafnium systems fail to yield cage compounds, generating instead trimeric species containing not only Cp* and oxo groups but also hydroxide and chloride ligands (see Scheme I). A preliminary account of the zirconium system has already appeared.[2] We provide here a full report of the synthesis, characterization, and solution stabilities of the four new complexes that have been prepared: $(Cp^*ZrCl)_3O(OH)_3Cl$ (**1**), $(Cp^*HfCl)_3O(OH)_3Cl$ (**2**), $(Cp^*ZrCl)_3O(OH)_4$ (**3**), and $(Cp^*HfCl)_3O(OH)_4$ (**4**).

[†] University of Illinois.

[‡] Crystalytics Co.